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Abstract
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SUBLIMATION OF ZIRCONIUM TETRAFLUORIDE

By
Louis J. Abate
Harley A. Wilhelm

March 1951

Ames Laboratory

Technical Information Service, Oak Ridge, Tennessee

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SUBLIMATION OF ZIRCONIUM TETRAFLUORIDE*

by Louis J. Abate and Harley A. Wilhelm

I. ABSTRACT

The demand for a dense zirconium tetrafluoride of high purity for use in the preparation of zirconium metal can be met by vacuum sublimation of zirconium fluoride prepared by the precipitation and dehydration method. Separation of zirconium fluoride from less volatile metallic impurities, moisture, and non-volatile zirconium compounds was accomplished in this manner. The degree of separation of the desired product improved with the use of lower sublimation temperatures; the lowest temperature was 750 degrees centigrade. Some fractionation from hafnium also occurred at this temperature, but zirconium tetrafluoride was the more volatile so a complete separation of zirconium from hafnium by sublimation does not seem practical.

Sublimations were carried out in vacuum covering the range from 750 to 1100 degrees centigrade. With a charge of 2000 grams and a sublimation time of 120 minutes which did not result in complete vaporization of the charge, the average rates of sublimation for the 120 minute period were: 8, 10.9, and 15.9 grams per minute for furnace temperatures of 750, 800, and 900 degrees centigrade respectively.

Using complete sublimation of the charge as the basis of comparison, an increase in the furnace operating temperature from 750 to 900 degrees centigrade decreased the time required from 360 to 150 minutes. An additional increase to 1100 degrees centigrade, however, only decreased the time for complete sublimation from 150 to 90 minutes, a relatively unimportant decrease in the total time for the operation.

The overall rate for complete sublimation of the charge varied linearly with temperature. A rate of 5.5 grams per minute was obtained with the furnace operated at 750 degrees centigrade and a rate of 22.1 grams per minute at 1100

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*This paper is based on an MS thesis by Louis Abate, submitted in March, 1951.

degrees centigrade.

A starting material containing very much less than the theoretical fluorine content greatly reduced the rate of sublimation. For a furnace temperature of 900 degrees centigrade and a sublimation time of 150 minutes, the sublimation of material having a fluorine content of 36 per cent gave a decreased yield of about 37 per cent.

Other studies made in a qualitative manner were: the effect of pressure on per cent zirconium fluoride sublimed, and materials of construction. At 900 degrees centigrade furnace temperature and a pressure during sublimation of 310 microns, a yield of 95.4 per cent zirconium tetrafluoride was obtained. Under the same conditions except for a higher pressure which was about 2000 microns, the yield was only 90 per cent. A yield of only 68 per cent was obtained when using the water aspirator for evacuation of the retort. As far as materials for construction are concerned, type 309 stainless steel with either monel or nickel lining and a condensing surface of monel or nickel seemed more satisfactory than the use of stainless steel itself which tended to flake and adhere to the sublimed product.

In view of the rate of sublimation, purity of product obtained, and time required, the optimum operating temperature would be about 800-850 degrees centigrade with a pressure of approximately 300 microns. At higher temperatures, the vapor pressures of the impurities become appreciable thus contaminating the product. With lower operating temperatures, the time required for complete sublimation increases rapidly.

II. INTRODUCTION

Choice of sublimation as a refining operation is sometimes dictated by the demand of the trade for a product of certain crystalline shape, density, and purity. In other cases sublimation offers particular advantages from the standpoint of ease of refining and economy or it may be resorted to in the refining of material which cannot be distilled without decomposition.

Zirconium fluoride for use in the zirconium metal reduction process must be of high purity. Various impurities in the finished metal cause poor nuclear properties, loss of corrosion resistance, or loss of ductility. The presence of oxygen in zirconium metal is very undesirable. Zirconium containing oxygen in excess of 0.2 per cent by weight can no

longer be cold rolled and shows a marked increase in hardness according to Lilliendahl (1). The hardness of zirconium metal has sometimes been used as a measure of the oxygen content of the metal.

Various attempts, using different methods, have been made at the Ames Laboratory of the Atomic Energy Commission to produce zirconium fluoride of a high degree of purity (2). The most satisfactory method thus far has been the wet precipitation of hydrated zirconium fluoride by the reaction of zirconyl chloride and 48 per cent hydrofluoric acid. This precipitate was air dried on a hot plate and then subjected to a high-temperature drying at 500 degrees centigrade in an atmosphere of anhydrous hydrogen fluoride. The zirconium fluoride produced by this method, however, still retained about 1 per cent of non-volatile material, probably zirconium oxide.

In order to prepare metal of a certain purity, one must first start with materials which are free of such impurities. Consequently, there arises the need of separating the fluoride from the oxide. Hevesy and Dullenkopf (3) reported that zirconium fluoride could be sublimed at 800-850 degrees centigrade under atmospheric pressure and 530 degrees centigrade in vacuum. Their report suggested the separation of fluoride from unconverted oxide by sublimation in which the oxide and other impurities less volatile than zirconium tetrafluoride will remain in the residue.

III. LITERATURE REVIEW

True sublimation from solid to vapor to solid is used in only a few cases. Pseudo sublimation, from solid to liquid to vapor to solid, is resorted to in the majority of subliming operations, because most substances do not exert sufficient vapor pressure velow their melting points to permit effective sublimation.

Movement of vapor in simple sublimation may be accelerated by operation under vacuum. If the total pressure on the solid in the vaporizer is reduced to a value below its vapor pressure by evacuating the apparatus through the condenser, spontaneous evolution of vapor occurs. Vacuum Operation, however, is not essential to obtain rapid vaporization. The partial pressure of vapor in the gas phase surrounding the solid may alternatively be reduced to a value less than the vapor pressure of the solid by passing an inert gas, commonly air, or steam over or through the solid in the vaporizer (4).

A secondary supply of inert gas is sometimes used for the purpose of condensing the sublimed vapors. This method of condensation is used when a fine pulverized product is preferred to the hard crystalline mass obtained by using a surface-type condenser. If desirable, the uncondensed vapors can be returned to the vaporizing chamber and the operation carried out in a closed cycle to prevent losses from incomplete condensation (5).

Fractionating operation of the vaporizing or, particularly, of the condensing chamber is employed in order to obtain an effective separation of materials such as the chlorides of iron and chromium (6). Generally, it may be said that if a pure product is directly obtainable by sublimation, this method of refining has some advantages; if, however, fractionating operations are involved and if the product can also be refined by distillation, the latter method is usually to be preferred.

Apparatus for sublimation are not so well standardized as in some other unit operations and are often specific for particular products or groups of products with which it may be used. For the most part, the apparatus for sublimation [(5), (7) through (17)] are constructed of glass and designed for laboratory use only.

The new type of sublimation apparatus reported by Kleipool (11) was used for purifying pyromeconic acid. This material was introduced into an annular channel surrounded by an oil bath which was electrically heated. Inside the channel was an opening connected to a flask, into which the sublimed product fell as it became detached from the water-cooled condenser located over the opening. The main feature of the apparatus was that the sublimed material does not drop back into the charge. Also, the operation need not be interrupted for the purpose of recovering the sublimate.

Pitha (12) described a simple sublimation apparatus which was used for the purification of selenium dioxide, arsenious oxide and phosphorus pentoxide. The vaporizer, which was constructed of pyrex tubing, was drawn at one end so that the vapors could be directed into a collecting tube and condensed on the wall. The collecting tube was easily detached so that the product could be removed by scraping.

Benvegnin (13) reported a sublimation apparatus which consisted of a condenser, a watch glass, a nickel dish, and a hot plate. In this apparatus the watch glass was placed under the condenser to collect the condensate. Likewise,

Nelson (14) used a screen a short distance below the condenser to catch any crystals of the sublimate that broke away from the condenser.

In a patent issued to Hansgirg (16), the inventor described a commercial size sublimation apparatus which was used in the refining of magnesium. The sublimation retort, when placed in the electrical resistance furnace, formed a gas-tight seal so that the furnace as well as the retort could be evacuated to avoid collapse of the retort at the higher temperature.

The vaporizing chamber in the retort was provided with means for controlling the speed of the vapor passing to the condenser. This consisted of a series of open-bottom, imperforate walled co-axially superimposed hollow members in the shape of truncated cones, which were so arranged as to leave a small space between each pair of the successive members. The uppermost member was surounted by a conical cap which had slots.

For charging the apparatus, a cover was provided at the top of the retort with an extension which was used for evacuating the retort. A tubular charging shaft was positioned to receive material introduced through this opening and direct it downwardly into the vaporizing chamber, being further assisted by a funnel-like member located between the vaporizing and condensing chambers. The condensing chamber consisted mainly of a split-type liner for ease in removing the condensate, which built up on the walls of the retort. The liner was provided with web members having holes for the purpose of receiving lifting hooks.

In its theory and fundamentals, [(18) through (22)] sublimation is analogous to distillation as far as vaporization is concerned, including application of the law of partial pressures. Thermodynamics as applied to sublimation has been given special treatment (18) and a new theory of the rate of sublimation and vapor pressure of solids has been advanced (19).

Duclaux (20), in his report, considered the vapor pressure of solids below the triple-point temperature. He also gave a formula which is claimed to represent accurately the vapor pressures of both liquid and solid at all temperatures. However the triple-point and critical constants must be known in order to use the formula.

Milosavlévic (21) also derived a relation between pressure and corresponding boiling temperature in terms of the critical pressure and the absolute temperature of the triple-point. This derivation, obtained by starting with the Clausius-Clapeyron equation, can be used to determine the relationship between pressure and sublimation temperature.

In so far as the needs for theoretical considerations are concerned, data for specific and latent heats, heats of sublimation, triple-point pressure, and vapor pressure over a wide range of temperatures for many substances are required.

Sublimation under vacuum is applied to advantage in some cases [(23) through (26)]. Recent developments in this field permitting operation under very low pressures have been used for large-scale production of metals, such as calcium and magnesium (24, 25). Veselovskii (26) reported the use of high-vacuum sublimation as a method of detecting and concentrating rare elements.

Kroll and his co-workers (27,28,29) reported that zirconium tetrachloride could be purified from iron, chromium, and zirconium oxide by subliming in a hydrogen atmosphere. The volatile ferric chloride was reduced to ferrous chloride by the hydrogen and was not volatilized at 500 degrees centigrade, the operating temperature of the furnace. The condensing surface was kept above 100 degrees centigrade to give the denser form of zirconium tetrachloride.

IV. MATERIALS AND EQUIPMENT

Several methods have been used at the Ames Laboratory of the Atomic Energy Commission to produce zirconium tetrafluoride. Material for the initial research on the sublimation of zirconium tetrafluoride was prepared by passing gaseous hydrogen fluoride over a bed of zirconium tetrachloride (2). This reaction was carried out in graphite trays at a temperature of 50 degrees centigrade. The fluoride made by the low-temperature hydrofluorination of zirconium chloride exhibited a tendency to hydrolyze with atmospheric moisture. This hydrolyzing tendency, however, was eliminated by further hydrofluorination in monel trays at a temperature of about 400 degrees centigrade. The zirconium tetrafluoride prepared by this method retained the impurities that were in the chloride, the iron content being some 2000 ppm.

Another limited source of material was obtained as a

result of research on the hydrofluorinating properties of zirconium oxide. This was prepared by heating purified zirconyl chloride in a quartz tube at various temperatures ranging from 200 to 500 degrees centigrade. The product was a fused oxide, with a variable chlorine content, which had to be crushed before hydrofluorination. After crushing, the oxide was then hydrofluorinated in monel trays at a temperature of about 400 degrees centigrade.

The bulk of the starting material for the research on sublimation, however, was made by the precipitation and dehydration method (2). To a weighed amount of purified zirconyl chloride was added the stoichiometric quantity of 48 per cent hydrofluoric acid giving four fluorine atoms per zirconium atom. Upon stirring this mixture, the zirconyl chloride first went into solution and immediately a precipitation of hydrated zirconium tetrafluoride was formed. The heat of solution, which was noticed by the rise in temperature of the mixture and the evolution of vapor, probably caused the precipitation. This precipitate was about three times as dense as the zirconyl chloride. About 70 per cent of the mother liquor was removed by decantation. This allowed the suspended carbonaceous matter, which was introduced by the acetone washing of zirconyl chloride, to be separated from the product. The mother liquor also contained impurities such as iron and other soluble chlorides and fluories. Further removal of the mother liquor was accomplished by vacuum filtration. The wet precipitate was then dried in platinum-lined copper trays at 110 degrees centigrade. Dehydration of the hydrated zirconium fluoride was accomplished by heating for eight hours in an atmosphere of anhydrous hydrogen fluoride at 500 degrees centigrade.

The equipment used for the experimental work consisted of three main units: the heating unit, the vacuum unit, and the sublimation unit. The combination of these three units is shown in figure 1.

The heating unit was composed of a gas-fired furnace, shown in figure 2, together with the control mechanism. The transite box (A), which directed the combustion gases to the flue, covered the retort support (B). This support rested on the furnace housing (C) which was constructed of rolled steel 36 3/4 inches high, 16 inches inside diameter and 24½ inches outside diameter with about 4 inches of dicalite insulation between. Heat was supplied by a 12 inch ring burner (E) above which was a reflecting tray (D) filled with magnesium oxide. A chromel-alumel thermocouple in the thermocouple well (F) was connected to a Whellco Capacitrol. The capacitrol in conjunction with a magnetic

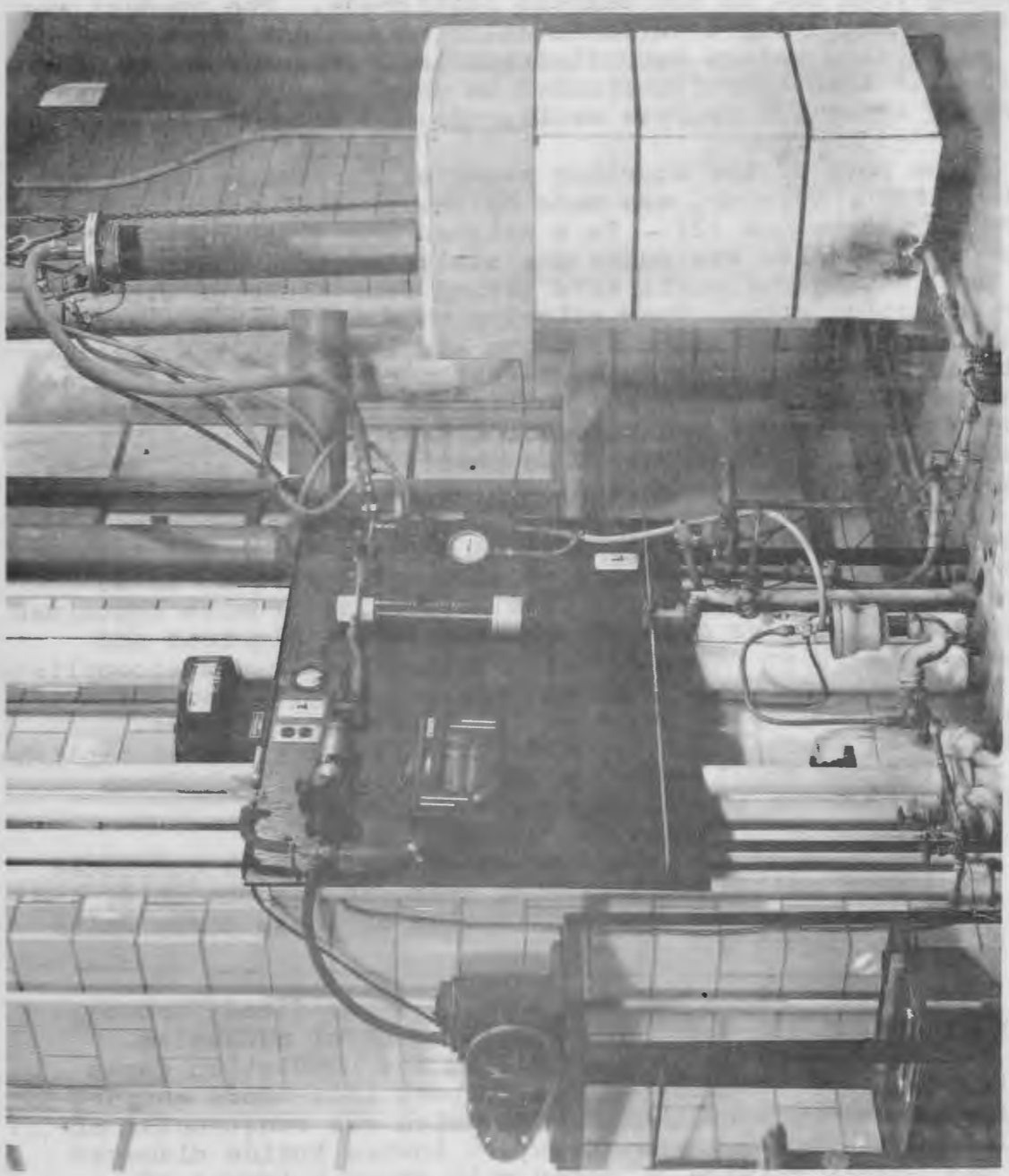

Fig. 1 General assembly.

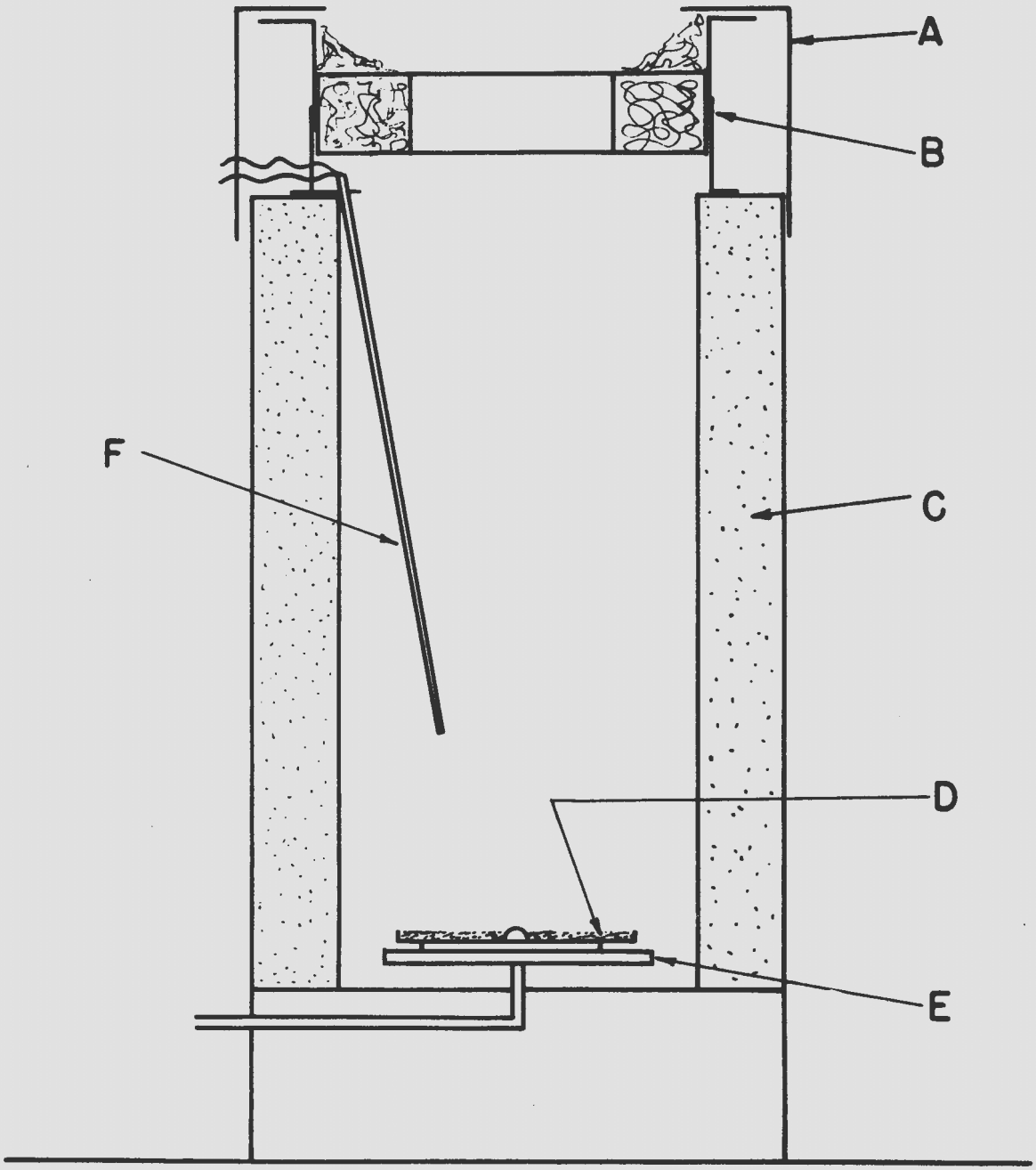

Fig. 2 Gas-fired furnace.

high-low control valve was used to control the furnace temperature.

Use of vacuum in a sublimation process increases the movement of vapor and makes possible the use of a lower temperature of vaporization. During the heating period of a sublimation run there was an evolution of hydrogen fluoride from the charge which caused corrosion and freezing of the mechanical pump. For this reason, the vacuum unit was composed of two parts. In the first part, a water aspirator was used for the initial evacuation of the system. A Bourdon-type gauge was used to indicate if the system was being evacuated; since the aspirator often tended to plug. The hydrogen fluoride fumes were allowed to pass through the aspirator to be diluted with the water.

The second part of the vacuum unit employed a Cenco-Pressovac 4 Pump to supply the higher vacuum. A Flosodorf-type Stokes McLeod gauge, which was used to measure the vacuum, was located close to the pump as shown in figure 1. To protect the pump from any additional evolution of hydrogen fluoride, a dry sodium fluoride trap and a calcium filled cold trap preceded the pump. The calcium trap, cooled by dry ice and trichloroethylene, was used to condense the fumes. After removal of the trap from the system, the condensate reacted with the calcium upon reaching room temperature. The anhydrous sodium fluoride trap was used to eliminate any hydrogen fluoride that may have passed beyond the cold trap. These two parts of the vacuum unit were connected to the retort through a tee so that either one or the other may be used by simply closing the pinch-type clamp on the part that is not wanted.

The sublimation unit consisted of a retort, an indicating pyrometer which was used to indicate the condenser temperature, and a Brown Electronic Potentiometer to record the temperature, of the charge in the retort. The initial work was carried out in a 2 inch stainless steel tube 26½ inches long with one end welded shut and the other end flanged. The first 6 inches from the flanged end of the retort had a water cooling jacket and an outlet to the vacuum pump. A removable flange plate provided a means of inserting and removing the 14 inch semicylindrical graphite tray which contained the charge. The retort was heated by placing it horizontally in an electrically heated furnace.

From the difficulty encountered in removing the sublimate from the retort which condensed on the sides, on scaling up the larger retort employed a cylindrical condenser (M) shown

in figure 3. This condenser, which was centrally located, was welded to the cover plate. The large retort differed from the small one in that it was operated vertically instead of horizontally and was heated by a gas fired furnace.

The retort (G) shown in figure 3 was constructed from 1/4 inch stainless steel type 309 in the form of a cylinder 5 inches inside diameter and 31 inches high. This was lined with sheet nickel (H). In order to protect the rubber gasket (I), several turns of copper cooling coils (J) were wound around the top 2 inches of the retort. To the removable top (K), cooled with cooling coils (L), was welded the vacuum outlet (O) and the 2 inch condenser (M) through which the thermocouple well (N) extended within 1/4 inch from the bottom of the retort. The condenser which was cylindrical extended 18 inches below and 1 inch above the cover plate.

The charge (P), approximately 6 inches deep, was placed at the bottom of the retort and was sublimed using baffle plates (Q) spaced 1 inch apart. The baffle plates served in reducing the mechanical carrying of impurities. The sublimed zirconium tetrafluoride (R) was collected on the condenser as shown.

V. METHODS OF PROCEDURE

Studies were made to find the effect of temperature on the rate of sublimation for zirconium tetrafluoride and on the purity of product obtained. From preliminary investigations, a standard procedure was evolved. The purity of product obtained was determined by chemical and spectrographical analyses.

A. Experimental

Into the nickel-lined retort (G), shown in figure 3, was charged 2000 grams of impure zirconium fluoride (P)and the baffle plates (Q) inserted above the charge. A rubber gasket (I), coated with celvacene vacuum grease, was placed on the flange. The removable top was then lowered onto the gasket and bolted to the retort. Necessary connections to the cooling water, cooling air, and thermocouples were made. These operations prepared the retort for the actual sublimation.

With the furnace controlling at the desired temperature, the retort was lowered into the furnace by means of a chain hoist as shown in figure 1. The water aspirator was then turned on in order to evacuate the system and remove the hydrogen

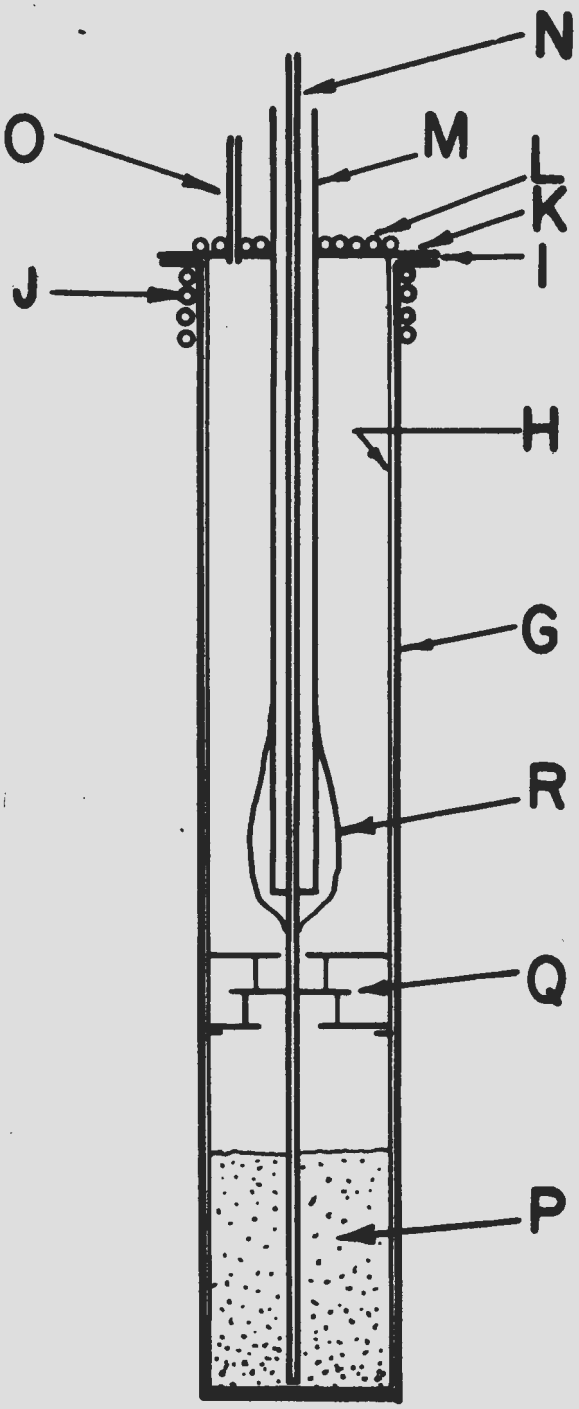

Fig. 3 Sublimation retort.

fluoride that was volatilized during the interval of time required for the retort to reach 650 degrees centigrade. This interval varied from 20 minutes with the furnace controlled at 1100 degrees centigrade to 120 minutes when the furnace was controlled at 750 degrees centigrade. Upon reaching 650 degrees centigrade, as indicated by the thermocouple in the bottom of the retort, the system was switched from the aspirator to the vacuum pump which initially had the rest of the vacuum unit evacuated to about 100 microns.

A drop in temperature of the charge in the retort, which indicated the start of sublimation, occurred shortly after the system was connected to the higher vacuum unit. This drop in temperature was about 25 centigrade degrees. Sublimation was then continued for a selected time which was varied from 90 to 360 minutes. At the end of such time, the retort was lifted out of the furnace, by means of a chain hoist, for rapid cooling. The interval of time beginning when the system was connected to the pump to five minutes after the retort was lifted out of the furnace was taken as the time of sublimation. Five minutes was added since it took approximately this length of time for the retort to cool below the sublimation temperature.

When the retort had cooled sufficiently to permit removal of the sublimate, the vacuum was broken by admission of air through a stopcock. The top cover and condenser assembly was then loosened and removed from the retort. The dense, hard, crystalline product was chopped off the condenser and collected in a plastic bag. Weights of this product and the residue in the bottom of the retort were obtained in order to calculate the rate of sublimation and the per cent yield.

The time required for a sublimation run of 2000 gram charge can be summarized as follows:

	time in minutes
preparation of retort for sublimation	40
heating retort to 650 degrees centigrade	20- 120
actual sublimation time	90- 360
cooling the retort to room temperature	120
removing the product and residue	30

Thus, the overall time required varied from 300 minutes for sublimations carried out at 1100 degrees centigrade to 670 minutes for sublimations at 750 degrees centigrade.

The sublimed zirconium fluoride was ground in a rubber-lined ball mill. This operation reduced the size of the

fluoride to a powder suitable for sampling and use in the zirconium metal reduction process.

B. Analytical

Chemical analyses of the original and sublimed zirconium tetrafluoride were necessary to ascertain the degree of purification that was possible through sublimation. Spectrographical analyses were obtained for some of the elements which could not be determined by chemical methods and to verify the results obtained from chemical data.

The methods for the determination of iron, nitrogen, nickel, and titanium were developed by Ayres (30). Zirconium tetrafluoride was treated with sulfuric acid in a platinum dish. Repeated evaporations to dryness removed fluoride ions until the dissolution of the samples was completed. The cooled solutions of the samples were then transferred to volumetric flasks from which aliquots were removed for the analysis of the individual elements. Each sample contained approximately 10 grams of zirconium.

An aliquot containing one gram of zirconium, with which values as low as 5-10 parts per million of iron in zirconium tetrafluoride can be determined, was treated with hydroxylamine hydrochloride to reduce the iron to ferrous iron. The addition of 1,10-phenanthroline caused the formation of the red ferrous sulfate-1,10-phenanthroline complex. The maximum color was developed at a pH of 5-7, which required the addition of ammonium tartrate to prevent the precipitation of zirconium. After a one hour interval to allow the color to develop, a portion of the solution was transferred to one centimeter cuvettes. The per cent transmission of the solution was determined in the Coleman spectrophotometer at 515 mμ with water as a reference. With the value found in this manner, the iron content of the solution was determined from a previously prepared standard curve.

Nitrogen was determined by the Kjeldahl method. Following the addition of tartaric acid and sodium hydroxide to an aliquot of the zirconium solution, steam was passed through the mixed solution until 50 ml. of the distillate had been collected in a solution of boric acid and methyl purple indicator which had been added to the vapor trap and receiver of the apparatus. The distillate was titrated with standard hydrochloric acid to a neutral gray end point. The necessary corrections for the indicator and reagent blank were made before calculating the nitrogen content of the solution.

An aliquot removed for the determination of nickel was

adjusted to a final pH of 8 after the addition of sulfosalicylic acid. About 10 ml. of this solution was used in a Sargent Model XII polarograph. Nickel appears at a half-wave potential of -0.95 volts measured against the saturated calomel cell. The instrument was calibrated by the standard addition method. Volumes of a standard nickel solution, containing approximately the same amounts as that found in the sample, were added to another aliquot of the sample. The mixture was given the same treatment as the original sample.

The colorimetric determination of titanium involved the formation of the yellow pertitanate ion by the addition of hydrogen peroxide to an aliquot of the zirconium sample in sulfuric acid. Using a sample containing one gram of zirconium, titanium can be determined as low as 10 parts per million in zirconium fluoride. The color was developed rapidly by the addition of hydrogen peroxide. The solution was transferred to a five centimeter cuvette and the transmittancy measured against water as a reference at 410 mμ in the Coleman spectrophotometer. Comparison with a previously prepared standard curve gave the titanium content of the solution.

Water in the zirconium fluoride was determined by an absorption method. A 5-10 gram sample of the fluoride was heated to 400 degrees centigrade for 3 hours in a nickel chamber swept out with dry nitrogen. After passage through the heating chamber, the gasses were passed through sodium carbonate at 300 degrees centigrade to remove the hydrogen fluoride and finally through a weighed magnesium perchlorate absorption tower where the water was absorbed. The gain in weight of the absorption tower minus the apparatus blank was used to calculate the per cent moisture in the fluoride.

The determination of carbon in zirconium tetrafluoride was made with a usual carbon train modified by having a scrubbing tower filled with a saturated solution of aluminum sulfate in 1:1 sulfuric acid to remove hydrogen fluoride. A glass wool plug was also inserted to filter the dust from the fluoride sample. An ignition at 1800 degrees fahrenheit for 45 minutes was required for the determination.

Vacuum sublimation at 575 degrees centigrade was used in determining the amount of non-volatile material in zirconium tetrafluoride. A 5 gram sample of fluoride weighed in a nickel boat was inserted in a vycor tube. The low temperature sublimation, which was carried out for one hour, reduced the amount of mechanical carrying. A cover plate placed on top of the boat also aided in this respect. The residue which remained in the boat was weighed and the per cent non-volatiles calculated.

The fluorine content of the starting material and sublimed product indicated the extent of oxide removal from the fluoride. The pyrohydrolytic method of Warf and Cline (31) was used to convert zirconium tetrafluoride into zirconium oxide and hydrogen fluoride. Steam was passed over the sample contained in a platinum boat heated to 800-850 degrees centigrade. The steam and hydrogen fluoride were condensed and collected in a silver dish. A titration of the distillate with standard sodium hydroxide in the presence of phenolphthalein indicator gave the fluorine content of the sample. In the case of sublimed zirconium fluoride, the pyrohydrolysis reaction took a long period of time to remove the last traces of fluorine.

The analyses for aluminum, calcium, copper, hafnium, iron, magnesium, nickel and silica were made by a spectrographic method which was under development. The oxide residue from the pyrohydrolysis of zirconium tetrafluoride was mixed with a special grade pelletting graphite, using 200 mg. of the oxide and 400 mg. of graphite. This mixture was intimately ground in a boron carbide mortar and then pressed in a briquetting press at a pressure of 160,000 psi. to form a $\frac{1}{4}$ inch pellet. This pellet was then excited with an over-damped condenser discharge from an ARL Multi-Source Unit. The spectrograph used was a Jarrell Ash 21 foot large grating spectrograph, exposures being made in the second order. Eastman Spectrum Analysis No. 1 plates were used and all densitometry performed with an ARL densitometer.

VI. EXPERIMENTAL RESULTS

The rate with which a compound is sublimed depends upon several factors, some of which are; temperature, pressure, and the amount of non-volatiles mixed with the compound, Vacuum sublimations were carried out to find the effect of temperature on the rate of sublimation for zirconium tetrafluoride and on the purity of product obtained. The effect of pressure and non-volatiles on the per cent sublimed were also investigated.

Before any actual sublimations were carried out, the equipment was checked for leaks. This was done by first evacuating the system and measuring the vacuum attained. A reading of 100 microns was considered satisfactory. If the reading was greater than 100 microns, then a search for the leak was made. The search was conducted by first pinching off the rubber vacuum tubing to the retort, then to the traps until the satisfactory reading was obtained. This procedure disclosed whether the leak was in the retort or in one of the traps. With the source of the leak narrowed down to either

the retort or one of the traps, this individual part was then subjected to internal air pressure and held under water. The leak was noticed by the escape of air bubbles from the water. Leaks in the system, which were few, usually occurred at the welded sections. Occasionally, one of the gasketed joints would be the source of the leak.

With the leaks in the system satisfactorily eliminated, the empty retort was then placed in the furnace in order to obtain some thermal data. Curves showing the temperature gradient inside the retort for various furnace temperatures are shown in figure 4. The inside retort temperature was lower then the furnace temperature due to the thermal resistance of the retort and liner. The location of the furnace thermocouple (F), shown in figure 2, coincided with the outside bottom edge of the retort. These thermal data were taken in order to assure that the retort was hot enough to prevent the vapors from condensing before reaching the bottom of the condenser, which was located 14 inches from the bottom of the retort. As a check, two sublimation runs were made with the furnace temperature lowered to 700 degrees centigrade. The results of these low temperature sublimations indicated that the retort was not hot enough since, the vapors condensed under the top baffle plate before ever reaching the condenser. Successful sublimations, however, were carried out with a furnace temperature of 750 degrees centigrade which was considered as the lowest temperature of sublimation that was possible with the equipment used. The highest temperature of sublimation was limited to the temperature which the furnace could attain. With the maximum and minimum operating temperatures fixed, sublimations were then carried out covering the range from 750 to 1100 degrees centigrade.

Generally, the process operates in such a manner that the volume of charge in the vaporizer is continually decreased as the charge is sublimed by heat passing through the walls and bottom of the retort. Because of the decrease in surface area from which heat is transferred by conduction to the charge, it is to be expected that the first part of the zirconium tetrafluoride would sublime more rapidly than the last part. Several runs were carried out at different temperatures to determine the magnitude of this effect. Figure 5 shows the effect of time on the per cent zirconium fluoride sublimed for furnace temperatures of 750, 850 and 900 degrees centigrade. Since the curves approach 100 per cent asymptotically, it follows that a relatively longer time is required in the latter stages of sublimation.

A decrease in the overall rate of sublimation with respect

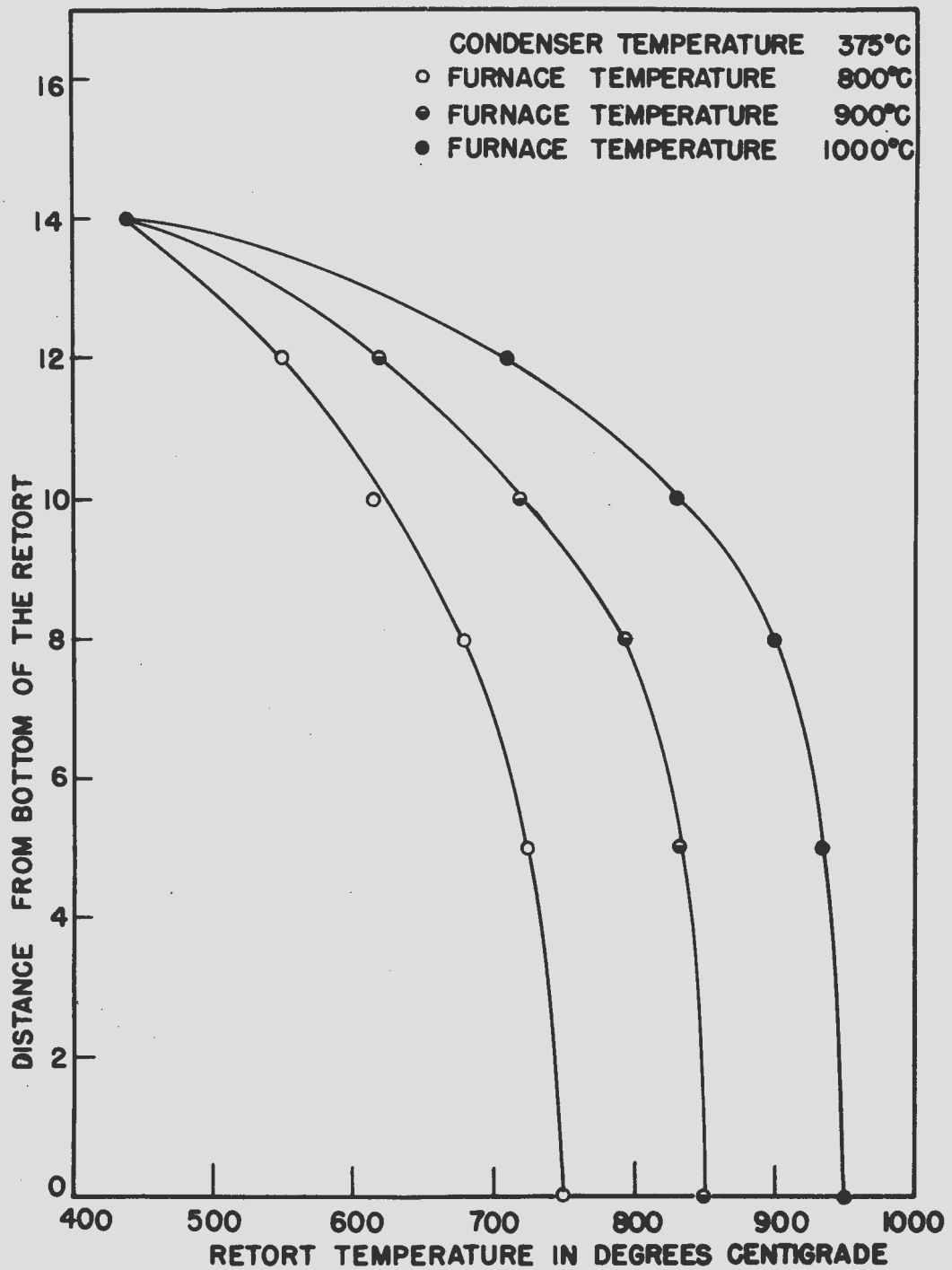

Fig. 4 Temperature gradient of retort.

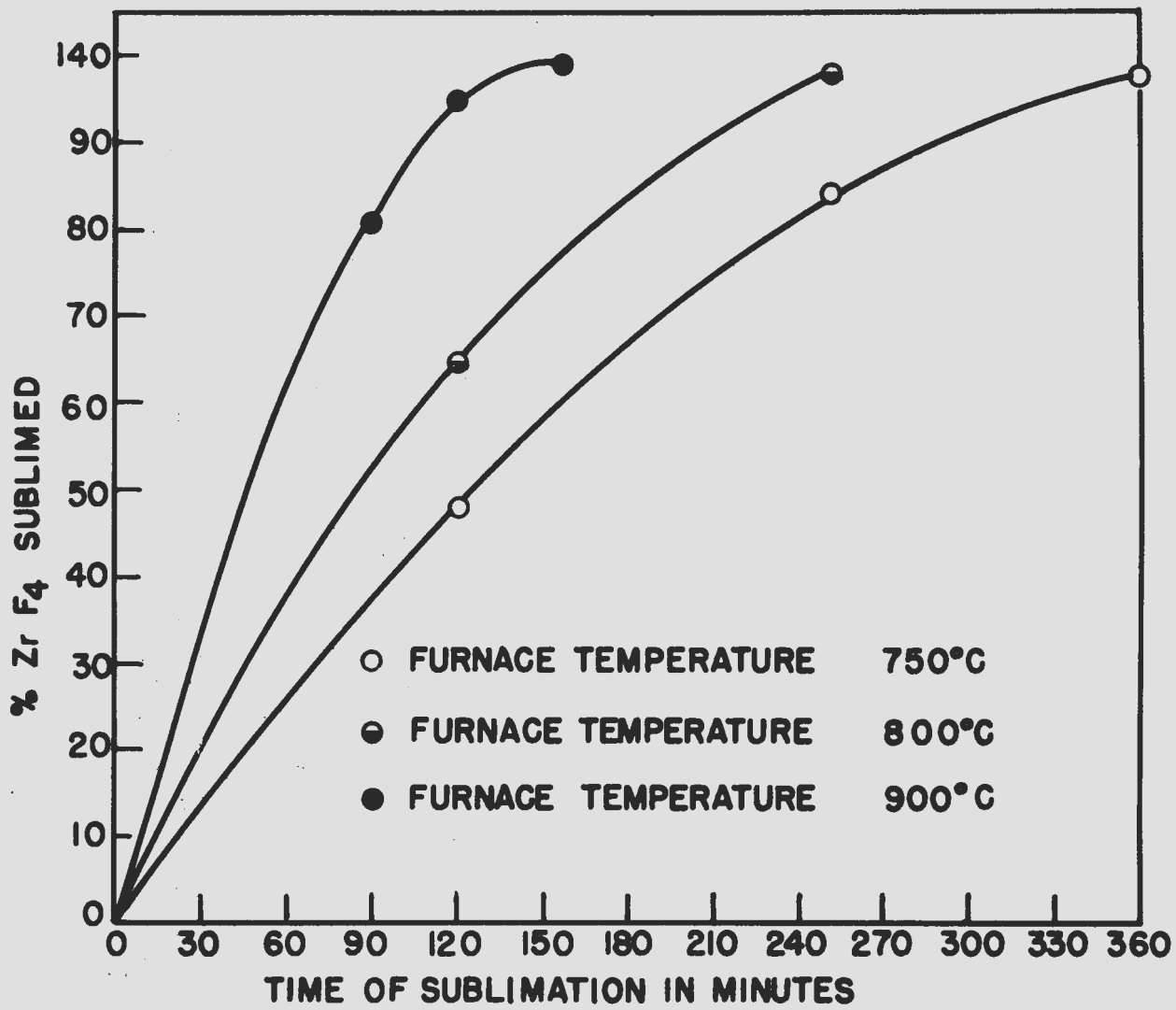

Fig. 5 Effect of time on per cent ZrF_4 sublimed.

to time is shown in figure 6. The overall rate was obtained by dividing the amount sublimed in grams by the time of sublimation in minutes. It should be mentioned that the starting material for the 90 minute sublimation run at 900 degrees centigrade was of larger particle size than the minus 60 mesh fluoride used for the other runs. However, this particle size effect on the overall rate of sublimation was apparently not too great and the points lie practically in a straight line. The amount of fluoride of this particular supply, however, was not sufficient to check the point in question.

As one would expect the rate of sublimation increases with temperature. From figure 6 we find that for a sublimation time of 120 minutes, the rates of sublimation are; 8,10.9, and 15.9 grams per minute for furnace temperatures of 750, 800 and 900 degrees centigrade respectively. It is apparent, that the rate of sublimation for a constant time does not increase linearly with temperature.

In order to carry out a sublimation operation efficiently, one should have some way of knowing when the vaporization of the charge is completed. If the vaporization is complete, continued heating of the retort would be a waste of both fuel and time. On the other hand, if only 50 per cent of the charge has been vaporized, stopping the sublimation would decrease its efficiency.

From the theoretical aspect of sublimation, we find that the phase change of zirconium tetrafluoride from solid to vapor for a given pressure and with a steady heat supply will proceed at a constant temperature. Therefore, it seemed feasible that if a thermocouple was placed in the charge; a recorder in conjunction with this thermocouple would record a constant temperature during sublimation and a rise in temperature at the termination of the run. This the purpose of the thermocouple well (N) shown in figure 3. This purpose, however, was defeated because the charge was not always in contact with the thermocouple well. During the heating period, the charge was sintered into a cake. Upon reaching the sublimation temperature, the zirconium fluoride began to sublime away from the thermocouple well and the walls of the retort. After about 20 per cent of the charge had sublimed, the temperature within the thermocouple well, which was no longer in contact with the charge, began to increase steadily due to the radiant heat coming from the bottom of the retort. Thus the expected sharp increase in temperature indicating the end of sublimation was not obtained.

Since the thermocouple well failed in its purpose, an

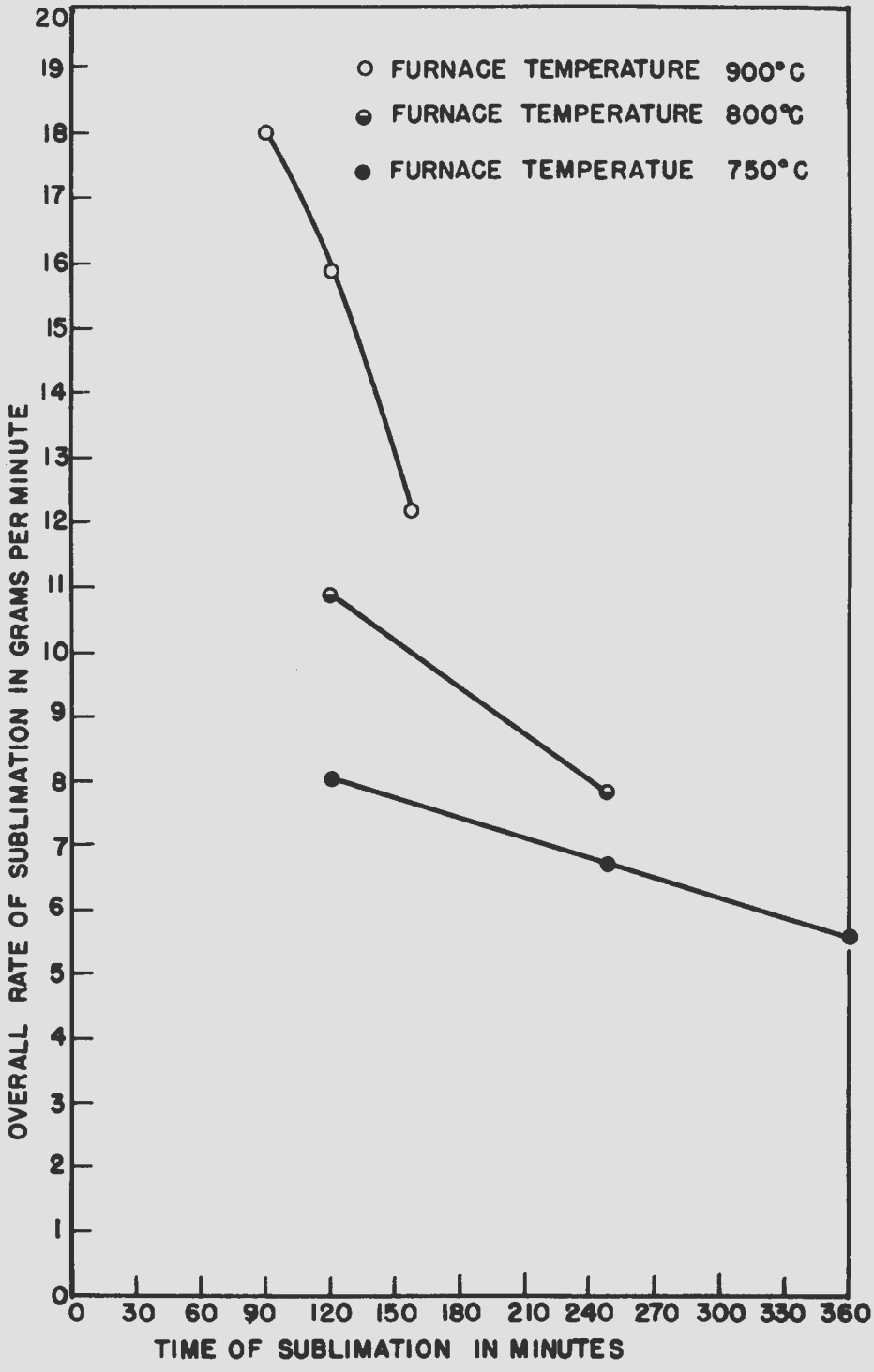

Fig. 6 Comparison of sublimation rate with furnace temperature.

extrapolation method was used in determining the furnace temperature at which vaporization will be complete in a given time. This was accomplished by calculating the per cent of the charge that was sublimed at various temperatures, keeping the time of sublimation and all other variables constant. An extrapolation to 100 per cent was then made in order to predict the temperature at which complete sublimation would result for the given time interval. A sublimation was then carried out at this temperature to verify the prediction. Table I shows the data for a series of runs that were made for 90 minutes and another series for 120 minutes. For the sublimation time of 90 minutes, 1100 degrees centigrade was the predicted temperature obtained by extrapolation and verified experimentally. Likewise, 980 degrees centigrade for the sublimation time of 120 minutes. Since the oxide content of the starting material was approximately 1 per cent the sublimation was considered complete when the amount of residue was down as low as 18 grams. The losses due to uncondensed gasses, such as hydrogen fluoride and moisture, and loss in handling were on the order of 0.7 per cent.

Using only the data from sublimation runs which resulted in complete vaporization of the zirconium fluoride, a plot was made of time versus temperature and is shown in figure 7. All of the sublimations were carried out using a charge of 2000 grams. It is seen, that an increase in the furnace operating temperature from 750 degrees to 900 degrees centigrade decreases the time required for complete sublimation from 360 minutes to 150 minutes. An additional increase of 200 centigrade degrees, however, only decreases the time from 150 to 90 minutes or a total decrease of 60 minutes. Therefore, it does not appear advantageous to operate at temperatures much above 900 degrees centigrade.

Figure 8, which was also plotted from data for runs resulting in complete sublimation, shows the overall rate of sublimation to vary linearly with temperature. The overall rate was calculated in the same manner mentioned previously. For the lower temperature ranges, this plot offers a more accurate extrapolated value than that of figure 7. If the straight line is extrapolated to 675 degrees centigrade, the corresponding overall rate of sublimation would be 2 grams per minute. From this rate, the time required for complete sublimation would be on the order of 17 hours. This compares with the low-temperature time of sublimation reported by Williams and Weaver (32).

With several runs which resulted in complete sublimation of the charge, the product obtained for furnace temperatures

Table I

Sublimation Yield for Constant Time

Time of Sublimation	Furnace Temp.(°C)	Grams of Sublimed ZrF	Per Cent Sublimed	Grams of Residue	Per Cent Residue
90 min	800	1090	54.5	880	44.0
90 min	900	1620	81.0	375	18.8
90 min	1000	1869	93.5	112	5.6
90 min	1100	1991	99.5	16	0.8
120 min	750	964	48.2	1020	51.0
120 min	800	1306	65.3	683	34.2
120 min	900	1908	95.4	88	4.4
120 min	980	1969	98.5	18	0.9

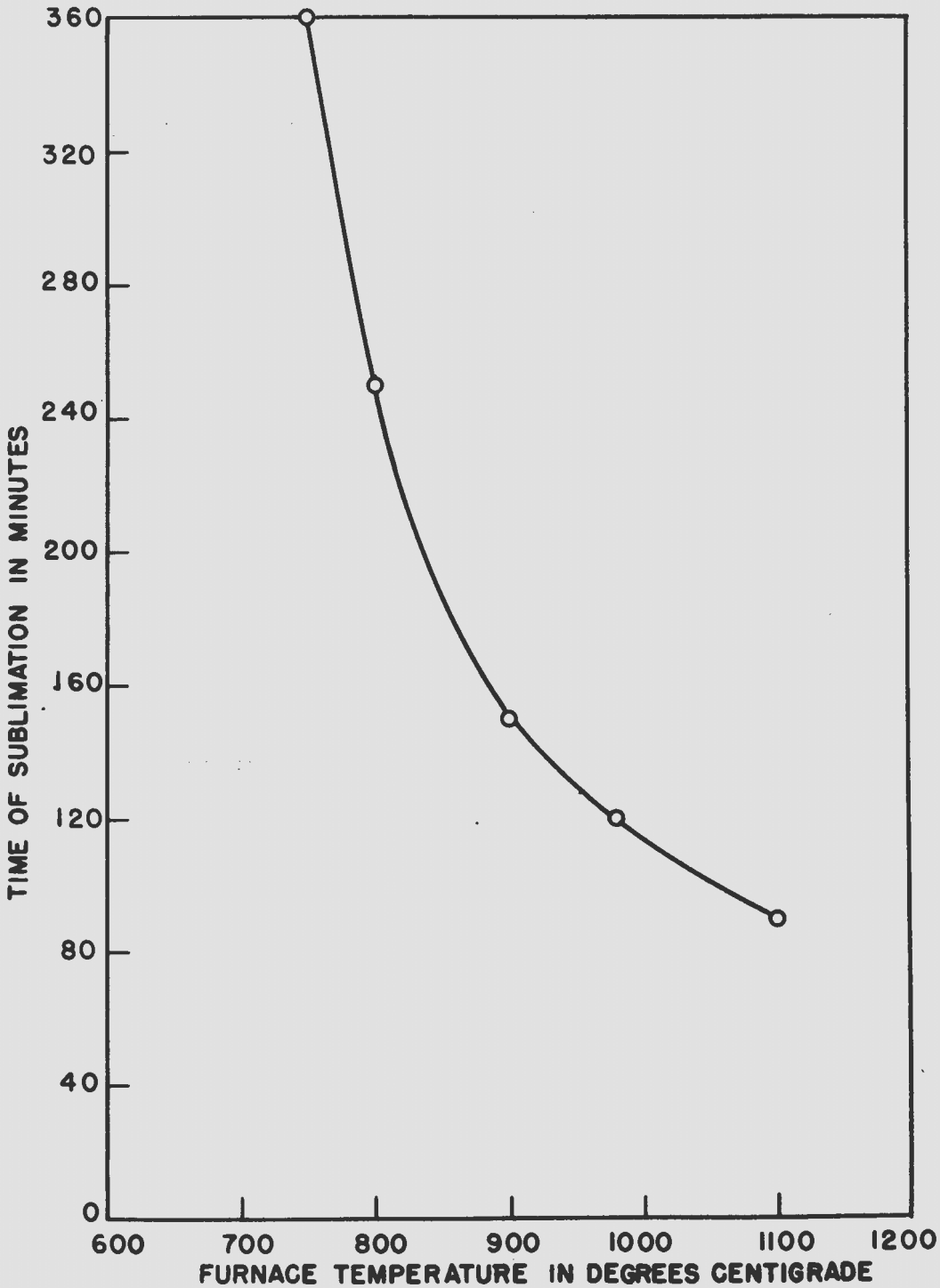

Fig. 7 Time-temperature relation for complete sublimation.

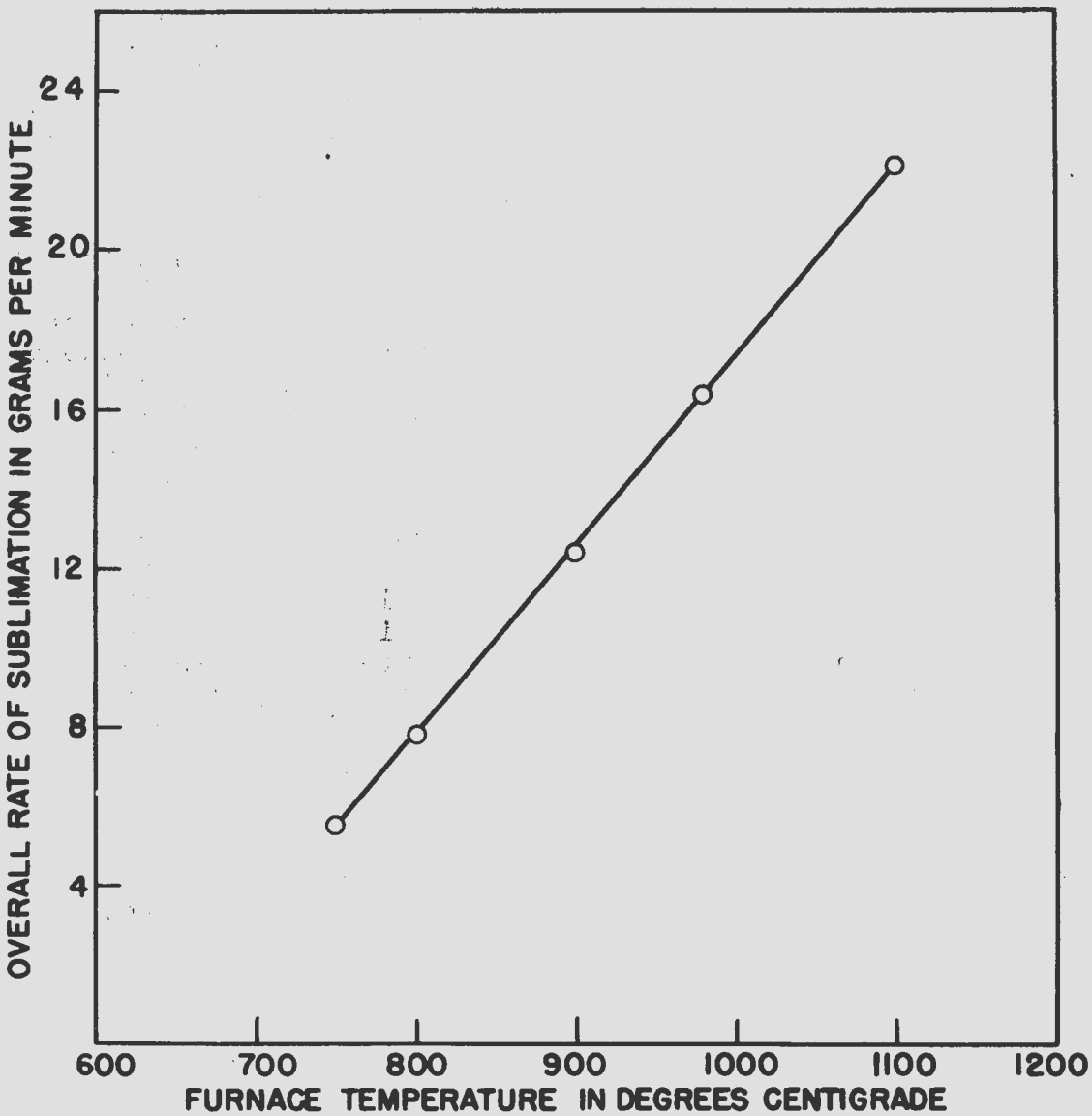

Fig. 8 Variation of sublimation rate with temperature.

of 750, 800, 900, 980, and 1100 degrees centigrade could now be compared by the analyses of the sublimed tetrafluoride. Table II shows the analyses of these products and also of the original zirconium fluoride which was used as the starting material. The analytical values determined by chemical methods are based on zirconium tetrafluoride; while, the spectrographical values are based on zirconium oxide. The fluorine content is indicative of the amount of zirconium that is present as tetrafluoride. For the theoretical value of 45.2 per cent fluorine, making allowances for impurities, all of the zirconium was considered to be present as tetrafluoride; while, a value of 44.8 per cent was considered to be due to the presence of uncoverted zirconium oxide.

From these analyses, it is apparent that a separation of zirconium from all of these impurities is possible with the exception of aluminum and silica. The high iron content of the fluoride sublimed at 1100 degrees centigrade is probably due to interaction of the vapor with the stainless steel retort. The most important separations are those of moisture and non-volatiles from the fluoride, since they would introduce oxygen into the zirconium metal and cause embrittlement.

It is noted that a greater hafnium-zirconium separation occurs at a furnace temperature of 750 degrees centigrade. This suggests, that there is a greater difference of the vapor pressures of hafnium and zirconium fluoride at the lower temperature than at the higher temperature. However, a complete separation of hafnium from zirconium by sublimation is not practical, since zirconium fluoride is the more volatile of the two.

Table III shows the reduction of iron, nickel, carbon, and copper content that was obtained by subliming a more highly contaminated fluoride. This run was made at 800-850 degrees centigrade in a larger retort of similar design, with the exception that a monel liner was used instead of a nickel liner. Both monel and nickel seem satisfactory as far as corrosion due to fluoride is concerned. Stainless steel, however, is not satisfactory when in contact with the charge and especially unsatisfactory as a condenser since, it tends to flake and adhere to the condensed fluoride; thereby contaminating the product.

The effect of oxide on the yield was next studied. Several sublimations were carried out at a furnace temperature of 900 degrees centigrade, keeping all variables constant except the quality of the charge. Since the layer of non-volatile zirconium oxide on top of the charge increases as sublimation

Table II

Effect of Sublimation Temperature on Purity of Product

Chemical Analyses	Original ZrF_4	Furnace Temperature (°C) 750	800	900	980	1100
Fluorine (%)	44.7	45.2	45.2	45.0	45.0	44.8
Moisture (%)	0.32	0.056	0.037	0.035	0.036	0.035
Non-Volatiles (%)	0.8	0.22	0.17	---	0.3	0.35
Fe (ppm)	18.7	12.1	12	17.8	19.9	145.3
N_2 (ppm)	71.3	24.7	16.0	20.3	19.3	10.7
Spectrographic Analysis						
Al (ppm)	145	125	120	125	120	115
Ca (ppm)	10	6	6	4	7	10
Cu (ppm)	20	4	5	5	5	6
Fe (ppm)	<100	<100	<100	<100	<100	1200
Mg (ppm)	~ 175	<175	<175	<175	<175	$\ll 175$
Ni (ppm)	82	64	72	85	90	150
Si (ppm)	<50	<50	<50	<50	<50	<50
Ti (ppm)	14	13	13	13	15	10
Hf:Zr (ratio)	2.1	0.65	1.9	2.0	2.1	2.1

Table III

Purity Obtained in Large Retort

	% Fluorine	Iron p.p.m.	Nickel p.p.m.	Copper p.p.m.	Carbon p.p.m.
Original ZrF_4	43.4	360	1970	200	180
Sublimed ZrF_4	44.9	40	190	20	16

proceeds, it is expected that the escaping tendency of the zirconium fluoride vapor from the charge would decrease with increasing amounts of oxide. Figure 9 shows the effect of unconverted oxide on the per cent zirconium fluoride sublimed. The per cent zirconium fluoride was based on the fluorine content of the charge; 45.2 per cent fluorine being considered as 100 per cent zirconium tetrafluoride. The pocrer quality fluoride was obtained from incompletely hydrofluorinated zirconium oxide. From the economic viewpoint, a starting material of fairly high fluorine content is more desirable, since the sublimation residue is not easily hydrofluorinated once it is heated to a high temperature such as that used in sublimation (2).

From theory, it would be expected that the lower the pressure the greater the rate of sublimation, since the vapor in equilibrium with the charge would be removed more readily. This effect of pressure, as expected, was confirmed by several runs which were made at 900 degrees centigrade, keeping all variables constant except pressure. For a pressure during sublimation of 310 microns, a yield of 95.4 per cent zirconium tetrafluoride was obtained. Under the same conditions except for the pressure which was about 2000 microns, the yield was only 90 per cent. A still smaller yield of 68 per cent was obtained when using only the water aspirator for evacuation of the retort during sublimation. As far as the effect on the appearance of the product is concerned, no relation could be found.

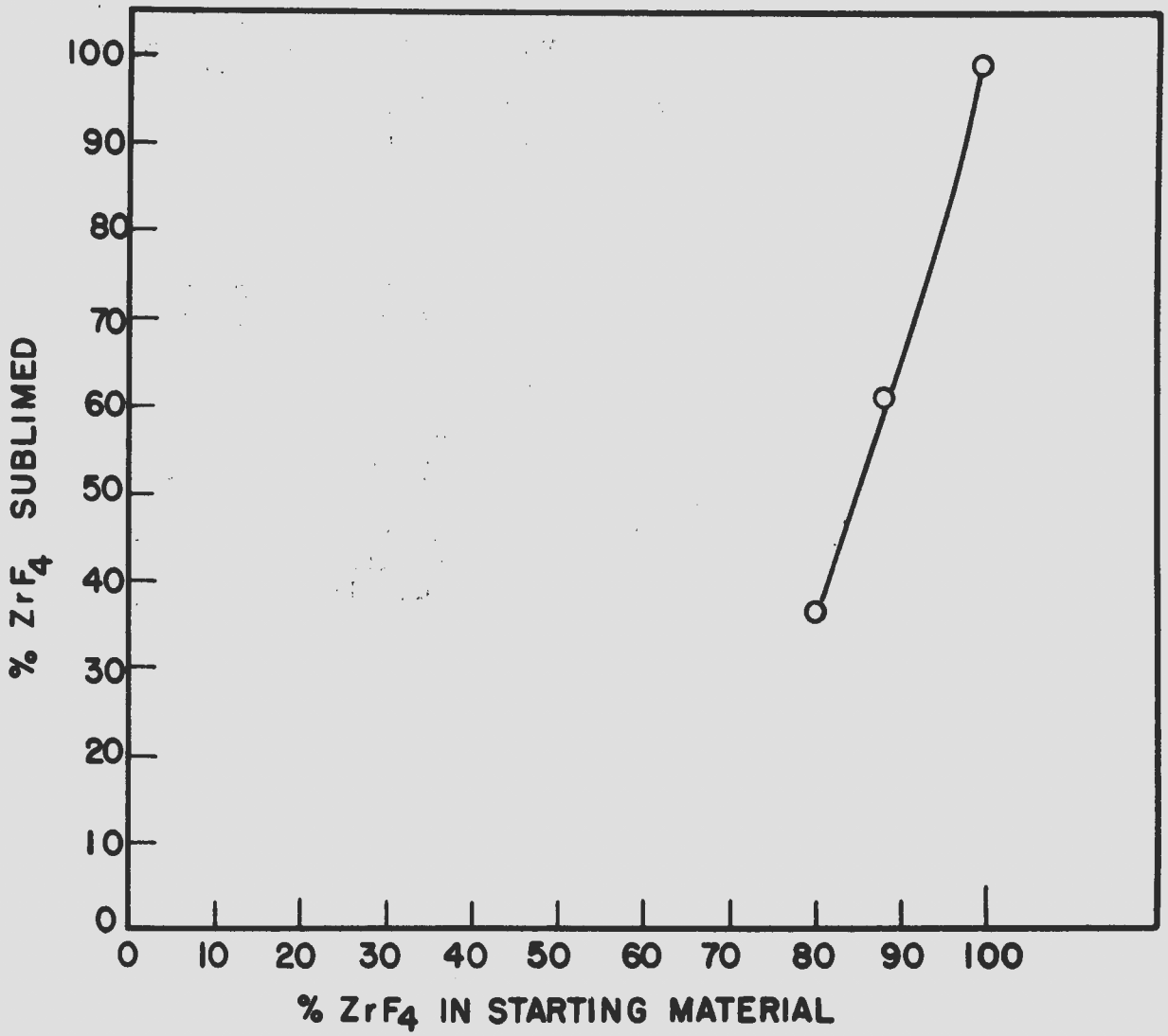

Fig. 9 Effect of oxide on yield.

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